Project Report: Mineral Biomarkers

Lead Team:	***Johnson Space Center***
Project Title:	***Mineral Biomarkers***
Project Investigator:	***Kathie Thomas−Keprta***

Project Progress

The aim of this project is the development of state−of−the−art instrumentation and accompanying protocols for analysis and detection of trace organic matter in terrestrial and astromaterials. Several independent approaches are being developed as outlined below:

Highlights for this review period include:

1. Two peer−reviewed manuscripts on ALH84001 magnetites were written (Thomas−Keprta K.L. Clemett S.J., Bazylinski D.A., Kirschvink J.L., McKay D.S., Wentworth S.J.,Vali H., Gibson, Jr. E.K., McKay M.F., Romanek C.S. (2001) Truncated hexa−octahedral magnetite crystals in ALH84001: presumptive biosignatures. *Proceedings of the National Academy of Science* 98, 2164−2169; Thomas−Keprta K.L., Clemett S.J., Bazylinski D.A., Kirschvink J.L., McKay D.S., Wentworth S.J., Vali H., and Gibson E.K., Romanek C.S. (2002) Magnetofossils from Ancient Mars: A Robust Biosignature in the Martian Meteorite ALH84001, *Applied and Environmental Microbiology*, in press).
2. A peer−reviewed manuscript on ALH84001 biosignatures was published (Gibson Jr. E.K., McKay D.S., Thomas−Keprta K.L., Wentworth S.J., Westall F., Steele A., Romanek C.S., Bell M.S., Torporski J. (2001) Life on Mars: evaluation of the evidence within Martian meteorites ALH84001, Nakhla, and Shergotty, *Precambrian Research* 106, 15−34).
3. A peer−reviewed manuscript describing experimental microbial fossilization by silificiation was published (Toporski J., Steele A., Westall F., Thomas−Keprta K.L., McKay D.S. (2002) The simulated silicification of bacteria−new clues to the modes and timing of bacterial preservation and implications for the search for extraterrestrial microfossils. *Astrobiology* 2, 1−26. *Winner of the 2001 Gerald A. Soffen Memorial Award*).

Evidence of biogenic activity on Mars has profound scientific implications for our understanding of the origin of life on Earth and its presence and diversity within the cosmos. Analysis of the Martian meteorite Allan Hills 84001 (ALH84001) revealed several lines of evidence that have led some investigators to suggest that microbial life existed on Mars approximately four Ga (billion annum) ago. One of the strongest lines of evidence is the presence of tens−of−nanometer sized magnetite [Fe_3O_4] crystals found within carbonate globules and their associated rims in the meteorite. This past year we made major progress in characterizing ALH84001 and biogenic MV−1 magnetite. Approximately one quarter of the ALH84001 magnetites have remarkable morphological and chemical similarities to magnetite particles produced by magnetotactic bacteria strain MV−1, which occur in aquatic habitats on Earth. Moreover, these types of magnetite particles are not known or expected to be produced by abiotic means either through geological processes or synthetically in the laboratory. We have therefore argued that these Martian magnetite crystals are in fact magnetofossils (see references in 1 above). If this is true, such magnetofossils would constitute evidence of the oldest life forms known.

In support of this interpretation we note that no experimental studies have produced, inorganically, magnetite identical to those generated by magnetotactic bacteria strain MV−1. The abiotic hypothesis of magnetite formation is based on the thermal decomposition of Fe−bearing carbonate to produce magnetite, with the implication that in ALH84001 such an event could have occurred through impact shock heating. Golden et al. (2002) have demonstrated that the decomposition of pure siderite [$FeCO_3$] can be produced in magnetite crystals with similar shapes and range of sizes to those found in ALH84001, although they have not been able to reproduce magnetites displaying the MV−1 magnetite geometry. Furthermore, several inconsistencies have yet to be addresses by the abiotic synthesis argument.

We are in the process of producing chemically simplistic analogs to the ALH8401 carbonates. Experimental work by Chris Romanek and colleagues at the Savannah River Ecology Laboratory shows that both magnetite and siderite can be produced at relatively low temperatures from aqueous solutions under CO2 partial pressure equal to that on Mars. These carbonates will be heated to produce magnetite that can be compared with those observed in ALH84001.

The first report of transmission electron microscope tomography of MV−1 magnetite crystals was discussed at the Lunar and Planetary Science Conference XXXIII (Thomas−Keprta et al., (2002)). This techqique confirms the MV−1 magnetite geometry originally proposed from classical TEM tilt imaging (see references in 1 above).

Recent work by Dennis Bazylinski and colleagues used off−axis electron holography in the TEM to characterize the magnetic microstructure of magnetotactic bacteria MV−1 and MS−1. One result was the unexpected finding that superparamagnetic magnetite in chains, while too small to retain stable magnetic moments if isolated, are influenced by the single domain magnetite nearby so that they behave like single domain magnetite. This explain how the ends of magnetic chains in magnetotactic bacteria, while often too small to have stable moments, can be influenced by the rest of the chain and can therefore contribute to the overall magnetic moment of the chain. Studies of submicrometer greigite (iron sulfide) show that its crystallization can be biologically induced or biologically mediated, and it is possible to tell the difference from the size distribution. Greigite may provide a suitable biomarker if it can be well characterized.

There has been discussion of the evidence supporting ancient microbial life within three Martian meteorites focused on biomarkers (see reference in 2 above). This work shows that while the search for evidence for extant life in ALH84001 continues, we have expanded our search to include other Martian meteorites as well.

Studies by J. Papike and M. Spilde of Mn−bearing precipitates in caves show that they are almost certainly formed by the action of Mn−oxidizing microbes. Diagenesis of amorphous and nanocrystalline Mn−oxides and hydroxides as well as biofilms form the mineral todorokite. Certain Mn−bearing minerals may make excellent stable terrestrial, and possibly Martian, mineral biomarkers.

Highlights

- New analyses of Nakhla Mars meteorite by double laser mass spectrometer show complex organics.

- Hopanes were detected by TOF−SIMs and we have begun standardization.

- Identification of organic compounds was made in 25 million year old fossilized bacteria?the first successful effort to combine morphologic and chemical biomarkers on fossilized bacteria.

- The use of fluorescent probes to acquire multiple types of information on single microbial cells or small colonies is being developed as an alternate to culturing for use as a life detection technique.

Roadmap Objectives

- ***Objective No. 6:*** Microbial Ecology
- ***Objective No. 8:*** Past Present Life on Mars
- ***Objective No. 17:*** Planetary Protection

Mission Involvement

Mission Class*	***Mission Name (for class 1 or 2) OR Concept (for class 3)***	***Type of Involvement*****
3	Sample Return	PI for sample studies

* Mission Class: Select 1 of 3 Mission Class types below to classify your project:

1. Now flying OR Funded & in development (e.g., Mars Odyssey, MER 2003, Kepler)
2. Named mission under study / in development, but not yet funded (e.g., TPF, Mars Lander 2009)
3. Long−lead future mission / societal issues (e.g., far−future Mars or Europa, biomarkers, life definition)

** Type of Involvement = Role / Relationship with Mission
Specify one (or more) of the following: PI, Co−I, Science Team member, planning support, data analysis, background research, instrument/payload development, research or analysis techniques, other (specify).

This project is key to understanding possible early life on Mars and therefore influences the design of Mars robotic missions, including the 2003 site selection for rovers, the 2007 in situ lander mission, and the 2011 sample return mission. In addition, it will influence the 2007 Scout missions. The presence of magnetotactic bacteria on early Mars has great implication for site selection, sample collection strategy, in situ analysis instrument selection, and confirming the presence of early oceans.

Based on the studies reported here, that some Mn oxides may be excellent biomarkers, we have new information on what to look for with the 2003 mission, the 2007 lander mission, possible 2007 Scout missions, and samples to be selected for return in 2011. If the Mn minerals found on Mars can be characterized well enough, they may tell us that microbes played a part in their formation

Cross Team Collaborations

We collaborate with the Carnegie Institution of Washington (Atomic Force Microscopy, Ion probe, and Raman Spectroscopy), and with the California Institute of Technology (squid magnetometer).